Small Scale Surveillance Sample Selection Plan

MIS Working Group Meeting
Savannah River Site
February 25, 2003

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LANL Shelf Life Surveillance Project

Small Scale Sample Study

Compile a shelf life surveillance database of the behavior of DOE material types prepared for storage.

- 10 g of oxide material in sealed containers where gaseous products and reactants are quantified over time
- Samples include: Site-wide representative oxide samples prepared to DOE Standard; Site-wide representative oxide samples prepared to bounding conditions; sample duplication; experimental duplication

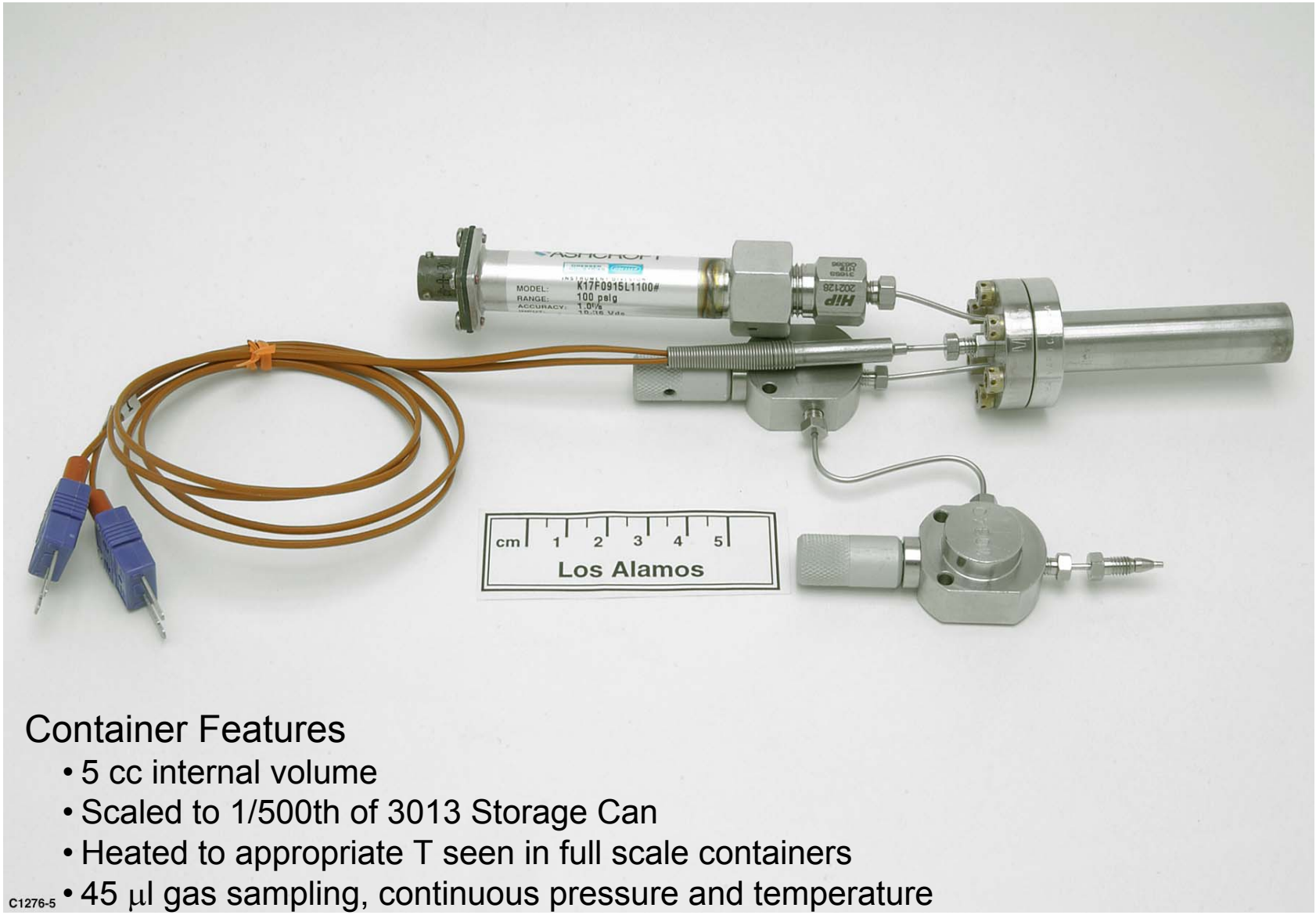
Full-Scale Study (work in parallel)

Establish baseline behavior of full- scale containers

Bound the behavior of material in extreme cases

- 5 kg of oxide material in 9 sealed 3013 BNFL inner containers

Small Scale Surveillance Experimental Design



Container Features

- 5 cc internal volume
- Scaled to 1/500th of 3013 Storage Can
- Heated to appropriate T seen in full scale containers
- 45 μl gas sampling, continuous pressure and temperature

C1276-5

Proposed small-scale sample breakdown for initial 45 locations

- Small Scale Sample Plan contains input from MIS Working Group
- Initial 6 months include sample blanks and sample replications
- Initial activities address gas generation and corrosion with of samples of pure oxide-moisture, and impure oxide-salts-moisture combinations in replicate
- Sample matrix is flexible and dependent on needs
- Annual data review will determine the termination of an experiment

Previous input from MIS Working Group

- **Samples should contain moisture (0.5 wt.% and higher)**
- **Include sample replication**
- **Include all the process sources from the packaging sites**
- **Select samples from large quantity items (>100g)**
- **Conduct TGA of samples**
- **Include the "cats and dogs" from the sites**
- **$Mg(OH)_2$ precipitation process samples**
- **Include parametric studies of pure materials and water**
- **Include parametric studies of oxides with high and low salt and high and low water content**
- **Do not examine MISNE4 (not representative)**
- **Include carbon source (ash or carbide) samples**
- **Include <30 wt.% Pu items (data for a variance if one is packaged)**
- **Develop a list of questions that each experiment addresses**
- **Integrate results with SRS and other surveillance activities**

Selection criteria based on perceived risk for container failure

Potential Concern	Parameter	Questions to be answered
Gas generation	water / pure oxide	What is the hydrogen generation rate, gas reaction kinetics, and established equilibrium pressure in pure materials?
Gas generation / corrosion	water / oxide / salts	What is the effect on pressure generation from potentially hygroscopic components in the oxide ($MgCl_2$ or $CaCl_2$)? Does HCl form and what is the effect on the container?
Experimental validation	Experimental and large scale duplication	Does the small-scale system behave the same as the full-size experiments? Does scaling down the experiment have an effect? Are results from identical samples experimentally reproducible? Are results from complex samples reproducible?
Gas generation-2	Calcination temperature Uranium oxide Fill gas Carbon source	Does a lower calcination temperature, result in more impurities and higher surface area oxide, affect the gas generation? Does uranium oxide act as a hydrogen sink? Does O_2 in air react with H_2 and limit the final equilibrium pressure?
Corrosion	Ga oxide	Does Ga oxide plate out on the container and cause a degradation concern for the container?
Other	process source low grade Pu oxide (<30 wt. %) One of a kind "cats and dogs"	Is there a process source that generates a concern? Are all included in the small-scale samples? Do samples that fall just outside the bounds of the 3013 standard behave differently than those at 30 – 80 wt. % Pu? Does unexpected behavior occur in materials that have not been examined because they exist in the inventories as a minority?

Start up activities to assure defensible data

- **Blanks:** Blanks will be done initially at each temperature setting then staged out as samples are loaded. At least one blank will exist at all times. Data for blanks initiated in non radioactive lab.
- **Duplicates:** Sample replication will be done initially on multiple samples for up to 6 months then reduced to duplicates upon review.

Small Scale Container Variables

- **Temperature**

  5 variable temperatures available (30-90^{o}C)

- **Moisture**
  - Moisture on materials as:
    - Hydrated salts ($CaCl_2 \cdot 6H_2O$ $MgCl_2 \cdot 6H_2O$)
    - Hydroxides ($Mg(OH)_2$)
    - Physisorbed water (on PuO_2)
- **Fill Gas**

  Majority will be filled with He; some will be filled with air

Small Scale Material Handling

MIS material that has been previously calcined to the 3013 criteria in the MIS program

- Sample for TGA-FTIR to determine adsorbed species on surface
- If material meets the 3013 criteria, then package in small scale container.

OR

- Heat oxide for 2 hours at ~225^{0}C* to remove adsorbed water without altering the chemistry of the material. (*If possible, examine TGA to determine temp.)
- Cool to room temperature
- Remove 10g into sample vial that minimizes headspace
- Transfer sample vial to a dry storage container for temporary storage prior to packaging in a small scale container

I.MIS material that has not been previously calcined to the 3013 criteria

1. Calcine for 2 hours at 950^{0}C
2. Protect sample from molecular readsorption

MIS material availability (see Table 2)

Current inventory contains items from:

- Process sources from RFETS, Hanford, LANL
- Material that was stabilized to 950^0C, 800^0C
- As received material
- Blended material
- Some small samples (<50 grams)
- Recombined materials following sampling or consecutive calcinations

Sample Plan (see Table 3)

- First batch of samples address reproducibility, gas generation in pure materials, and corrosive conditions in salt container materials

  PEOF1 - pure oxide / moisture
  large scale Can 1; well characterized material
  7 samples: dry (1); 0.5 wt.% H_2O (5), 2.0 wt.% H_2O (1)

  ARF-102-85-223 - impure oxide (64 wt.% Pu) with 5.5% Cl, 1.5% Na and 2% K
  7 samples: dry (1); 0.5 wt.% H_2O (5), 2.0 wt.% H_2O (1)

- Second batch of samples are further studies with same focus

  Pure oxide / moisture: 5501579, BLO-39, PBO-47

  Impure oxide / salts / moisture: ARF-295, C00695, 053038, 520610020

- Third batch of samples: $MgOH_2$ ppt process source R437, R440
- Fourth batch of samples: Pu-U oxides / moisture

  Pu, U oxide / moisture: PSU-84-06-05, 5501407, SCP711-46, ARF-355